# White Paper

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# White Paper to the National Endowment for the Humanities

**Grant no. PR-234484-16**

**Project: Effects of relative humidity fluctuations on paper permanence**

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This project was aimed at expanding our understanding of the damaging effects of cycling humidity environments on paper, which we had observed in earlier experiments. To broaden our view, we planned to study several different types of papers: unsized, mildly acidic cotton; sized alkaline book paper made with wood pulp; and acidic groundwood in two different newsprint papers. Four different relative humidity conditions were created (three cycling and one static) at room temperature in a custom apparatus. In addition to the rapid cycles from very low to very high humidity, which was the condition in our earlier experiments, we also created humidity cycles of slower frequency and with smaller excursions, which simulate environments of higher degrees of control.

The primary activities during the grant period were the construction of the exposure apparatus, the exposures of the test papers, and the analysis of the changes that resulted in the physical and chemical properties of the papers. Of these properties, the key ones were those that would affect the permanence and durability of the papers: the tensile strength, both of the sheets and of their constituent fibers; the moisture content, related to the flexibility of the paper; the molecular weight of the cellulose, an indication of remaining useful life; the pH, a measure of the intrinsic instability to chemical degradation; and the color. Only the molecular weight of the cellulose in the book papers could not be measured. These sheets were sized by the chemical bonding of a polymer to the fibers, and this sizing agent could not be removed without affecting the molecular weight values we sought to obtain. As reported below, however, the lack of these data were not critical, since none of the other measured properties for the book papers were significantly altered from the humidity exposures, so it was unlikely we would have observed changes in the cellulose molecular weight.

Adjustments were made to the original experimental plan as we proceeded. At the start, rather than test all the papers in one exposure, we deemed it preferable to test the very absorbent cotton papers and the newsprint in separate six-month exposures. As we gathered early results during the exposure of the cotton and book papers, however, we decided to continue the exposure of those papers in order to characterize more fully the behaviors of those critically important media. In making this decision, our examination of the behavior of the newsprint papers was necessarily abridged, with only a single test of the reaction to the most severe of the RH cycles after six months of exposure. While not thorough, that first look at the reaction of the newsprint papers resulted in some interesting results that should be explored further in future experiments.

***Experimental findings***

A twelve-month exposure was completed for the cotton and book papers, with samples tested every month or two, and a six-month exposure to the rapid extreme cycling condition was performed for the two newsprint paper types, with measurements taken at the start and end of that exposure. Color measurements were taken but are not reported for the cotton and book papers, since no significant color changes (color differences greater than 1) occurred.

The results we obtained allow a more complete description of the effects of cycling humidity on paper. Three findings are of particular importance. First, we have observed once again the

deleterious effects of wide, rapid humidity cycles on the strength of unsized, mildly acidic cotton paper, the behavior we discovered in our prior experimental work. In this experiment, ***the cotton paper lost about 40% of the tensile strength of the sheet and of its constituent fibers, and this strength loss was a result of a significant decrease of the molecular weight of the constituent cellulose***. Importantly, there was no evidence that the other properties of the paper – its pH, moisture content, or color – were altered measurably. As we had observed before, the exposure to rapid extreme humidity cycles seemed to result in paper that was very weak, yet otherwise unaltered in its appearance or intrinsic chemical stability (over the short term).

Another important finding is that the other humidity cycle conditions also produced some smaller degree of strength loss, but the effects of the smaller humidity variations (45%-55%RH) and of the slower large fluctuations were not significantly different than those produced by exposure to the steady 50% RH condition. This could simply be a reflection of the normal slow degradation of an acidic paper. ***It seems that these less severe cycling humidity environments of smaller or slower excursions had no aggravating influence on the degradation of the acidic cotton paper***.

The third major conclusion of the experiment is that ***the sized alkaline book paper was unchanged in exposures to the same humidity cycling conditions that affected the cotton paper***. No strength decreases were observed, and the pH, moisture content, and color were similarly unchanged throughout the exposures. (As mentioned above, the cellulose molecular weight could not be determined because of the interference of the non-cellulose constituents of this paper. It would be expected, however, that the cellulose would show no significant reduction, since that would likely be reflected as a change in tensile strength.) The reason for this difference with the cotton paper cannot be specified, since several key composition variables were different for the book paper: it is made with wood pulp, it is sized, and it is alkaline. Wood fibers might react differently than cotton to moisture content cycling. The sizing could act as a buffer to ambient humidity changes, or the sizing materials could act as a structural reinforcement to reduce physical distortion of the fibers or paper web. And the alkaline pH will naturally reduce dramatically the intrinsic rate of cellulose degradation by hydrolysis reaction, so even if humidity cycling should have some accelerating influence, it may not speed the rates enough to be significantly different. Further experimental work would be needed to identify the reason for this resistance to humidity cycles displayed by the book papers.

Finally, our examination of the effects of cycling humidity on newsprint was necessarily preliminary, for reasons described above. But the findings even at this stage seem to indicate important similarities and differences with the cotton and book papers. The strength of the sheets and of the fibers in the two newsprint papers seem to decrease slightly over the six-month exposure to rapid wide humidity extremes. Yet these possible changes are still not greater than the standard deviations of those measurements, and there is no control sample exposed to steady humidity, so no firm conclusions can be drawn. Nevertheless, one can observe that ***there is no evidence in the newsprint samples of the large strength loss that was observed under these humidity conditions in the cotton papers***. The only other finding that is remarkable is the results of color changes in the newsprint papers exposed to these severe cycling humidity conditions.

Unlike the cotton and book papers, which demonstrated no color change great enough to be perceived, ***the two newsprint samples did show evidence of color shifts***, with color differences of 1.5-2 CIELAB units. Interestingly, the color shifts in opposite directions for the two newsprint papers, as indicated by the ΔL* and Δb* values, and by the ASTM Yellowness Index: Newsprint 1 bleaches slightly, while Newsprint 2, the more yellow of the two papers, becomes slightly more yellow from the humidity exposures. These findings were unexpected (although discoloration from humidity cycles motivated some of the earliest work in this area), and the origin of such color shifts is unknown. Further research could aim to discover the color reactions at work in these papers.

***Outlook***

As is common for most research efforts, our experimental findings prompt new questions, and these could be important ones to address. Are acidic papers alone at risk in uncontrolled humidity environments? Will color shifts occur for groundwood papers, and to what extent is the widespread occurrence of yellowed groundwood paper in collections a result, at least partly, to exposure to uncontrolled humidity environments? Additional research, perhaps aimed at archival materials on low-quality paper rather than on book papers, might be needed.

Another way in which this research can be further developed is to explore humidity changes that simulate more closely the environmental conditions within books, paper stacks, and boxed materials, rather than room environments. The research that has been done regarding these microclimates emphasize the role of temperature changes in driving moisture into and out of papers, and these conditions could also be simulated easily with the apparatus we have constructed. This examination of the possible mitigation of humidity-induced degradation would seem to be especially important.